PATENT ABSTRACTS OF JAPAN

(11)Publication number:

2001-082682

(43)Date of publication of application: 30.03.2001

(51)Int.CI.

F16L 59/02

CO8G 18/40

CO8J 9/00

(21)Application number : 11-257041

(71)Applicant: MATSUSHITA REFRIG CO LTD

(22)Date of filing:

10.09.1999

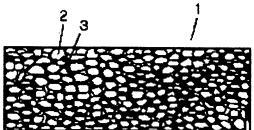
(72)Inventor: UEKADO KAZUTO

(54) HEAT INSULATING MATERIAL AND HEAT INSULATING STRUCTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a heat insulating material and a heat insulating structure capable of securing strength even when binder content is small, displaying heat insulating performance of high performance as a vacuum heat insulating material, preventing deterioration of performance even when it is perforated and excellent in practical workability.

SOLUTION: It is possible to provide a heat insulating material 1 of . high performance as a binder 3 which is a reinforcing material can be reduced and as a result, an excellent heat insulating characteristic of a urethane aero gel granular body 2 becomes dominant as rigidity is impoved by using a urethane aero gel having high bridged density urethane bonding with the urethane aero gel granular body 2 mixed and solidified with organic polyisosianate as the binder 3.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The heat insulator characterized by carrying out reaction solidification of the aerogel grain which consists of an organogel constituent which has the mesh structure of cross linkage of a three dimension in the molecular structure with the binder which consists of an organic material.

[Claim 2] The heat insulator which mixes the organic poly isocyanate as a binder to the aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and is characterized by carrying out reaction solidification.

[Claim 3] The heat insulator according to claim 2 with which it makes it come 2 to 15% to aerogel grain to mix the organic poly isocyanate.

[Claim 4] It is a binder to the aerogel grain obtained between an inner plate and a shell plate by drying the organogel constituent which has a urethane bond in the molecular structure. Thermal-protection-structure object which arranges the heat insulator which mixed the organic poly isocyanate and carried out reaction solidification, and really comes to foam to rigid urethane foam among said both plates.

[Claim 5] The thermal-protection-structure object characterized by being filled up between an inner plate and a shell plate after mixing the aerogel grain and the rigid-urethane-foam raw material which are obtained in the molecular structure by drying the organogel constituent which has a urethane bond.

[Claim 6] The thermal-protection-structure object characterized by having enclosed with the nonwoven fabric the aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and arranging it between an inner plate and a shell plate.

[Claim 7] The thermal-protection-structure object of six given in any 1 term from claim 4 equipped with penetration objects, such as a nail, piping, and wiring.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the thermal-protection-structure object which comes to arrange the heat insulator used for a residence, an incubation heat insulation device, etc., and a heat insulator. [0002]

[Description of the Prior Art] In recent years, high performance-ization of a heat insulator serves as a very important theme from a viewpoint of energy saving. Especially, by the residence or the incubation heat insulation device, efficient use of the heat energy by heat insulation occupies the big ratio in energy saving, and various measures are made to the improvement in heat insulation property of the heat insulator to constitute. [0003] In order to acquire the large energy-saving effectiveness especially, the attempt which is going to obtain the engine performance beyond twice is also made to the heat insulation property of the rigid urethane foam in the level which was excellent as a general-purpose heat insulator. They are the vacuum insulation material which decompressed the interior and specifically controlled the effect of gas heat conduction sharply, and the aerogel heat insulator with which it micropore-ized to the distance between openings below the average free process of air, and ordinary pressure also reduced gas thermal conductivity sharply.

[0004] For example, about vacuum insulation material, the core material which consists of detailed inorganic powder tends to be housed with a film-like plastic envelope, reduced pressure closure of the interior tends to be carried out at 1mmHg, and it is going to improve to about 2 times [of rigid urethane foam] heat insulation property by effect reduction of gas heat conduction as shown in JP,2-33917,B.

[0005] Moreover, an aerogel heat insulator includes silica aerogel with a binder, as shown in an EP-A -340707 [No.] official report, and it has the distance between openings below the gas mean free path of air, and the heat insulator which reduced gas thermal conductivity sharply is proposed.
[0006]

[Problem(s) to be Solved by the Invention] In vacuum insulation material, it cannot be overemphasized that it is required in the improvement in heat insulation property to carry out reduced pressure maintenance of the interior as JP,2-33917,B is shown. since [however,] jacket material consists of plastic envelopes -- heat -- getting damaged -- bag tearing might be carried out, like the electric water heater which is an incubation device, the nail was struck after use near the heater, or construction, and there was many accident from which a vacuum break arises by laminate film penetration in the example used as a heat insulator for residences with which post-construction of letting piping pass is added. Thus, in order to apply a heat insulator broadly industrially, the high performance heat insulator which can be equal to various construction from a viewpoint of dependability is indispensable.

[0007] On the other hand, since inorganic silica aerogel is used and there is no mesh structure of cross linkage of a three dimension into the molecular structure fundamentally in aerogel although binder content is made below into 50% volume for utilizing the engine performance of aerogel, and reservation on the strength as shown by the EP-A -340707 [No.] official report, it is difficult for there to be no rigidity and to reduce a binder sharply substantially. For this reason, there is a problem from which only about the same heat insulation property as glass wool is obtained in response to the bad influence of a binder.

[0008] Even if it penetrates, it offers a heat insulator and a thermal-protection-structure object excellent in practical use workability without performance degradation, while reservation on the strength can do this invention and it can demonstrate the heat insulation property of about the same high performance as vacuum insulation material in view of the above-mentioned technical problem, even if binder content is small.

[0009]

[Means for Solving the Problem] In order to attain this purpose, this invention is considered as the following configurations.

[0010] Since the heat insulator concerning claim 1 of this invention carries out reaction solidification of the aerogel grain which consists of an organogel constituent which has the mesh structure of cross linkage of a three dimension in the molecular structure with the binder which consists of an organic material, and the high organogel constituent of crosslinking density is used, rigidity becomes high.

[0011] The heat insulator concerning claim 2 of this invention mixes the organic poly isocyanate to the urethane aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond as a binder, and it is made to solidify it.

[0012] Since rigidity becomes high by using the urethane aerogel which has the high urethane bond of crosslinking density according to this invention, the binder which is reinforcing materials can be reduced sharply, the heat insulation property which was excellent in urethane aerogel grain as a result becomes dominant, and the heat insulator of high performance is obtained.

[0013] Moreover, the thermal-protection-structure object concerning claim 4 of this invention arranges said heat insulator in the interior of the structure which consists of an inner plate and a shell plate, and it really comes to foam on it from a rigid-urethane-foam raw material.

[0014] It can cast as a thermal-protection-structure object, without crushing aerogel by the blowing pressure force, even if it really foams by rigid urethane foam since the rigidity of said heat insulator obtained is high according to this invention. There is also no generating of the non-filling section from which inhibition of the restoration nature by collapse of the aerogel on the way of foaming becomes a cause especially, and high heat insulation property can be demonstrated as a thermal-protection-structure object.

[0015] Moreover, after the thermal-protection-structure object concerning claim 5 of this invention mixes the aerogel grain and the rigid-urethane-foam raw material which are obtained in the molecular structure by drying the organogel constituent which has a urethane bond, it carries out impregnation restoration and really comes to foam between an inner plate and a shell plate.

[0016] Since homogeneity can be made to distribute the aerogel which has the outstanding heat insulation property in the heat insulation structure according to this invention, the outstanding heat insulation property can contribute to the whole thermal-protection-structure object.

[0017] Moreover, the thermal-protection-structure object concerning claim 6 of this invention encloses with a nonwoven fabric the aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and is characterized by arranging between an inner plate and a shell plate.
[0018] According to this invention, since the rigidity of aerogel is high and it is not crushed by vibration etc., it is usable as a heat insulation member at configuration maintenance of extent put into a nonwoven fabric. Moreover, from heat-resistant height, even when the heater section is near the insulated hot-water-storing container, there is no constraint of a covering surface product and it can be covered to near the heater section. Consequently, when it is used for an incubation hot-water-storing container like an electric water heater, it is possible to demonstrate the outstanding heat insulation property by high coverage, and it can contribute to energy saving.

[0019] Moreover, the thermal-protection-structure object concerning claim 7 of this invention is characterized by penetration objects, such as a nail, piping, and wiring, being arranged by the thermal-protection-structure object.

[0020] According to this invention, aerogel consists of micropore below the average free degree of air, and in order to demonstrate the heat insulation property excellent in ordinary pressure, even if the exterior, a through hole, etc. are in aerogel, heat insulation property does not change. For this reason, it has the outstanding heat insulation property, without spoiling the function of penetration objects, such as a nail, piping, and wiring. [0021]

[Embodiment of the Invention] Reaction solidification of the heat insulator of this invention according to claim 1 is carried out with the binder which becomes the aerogel grain which consists of an organogel constituent which has the mesh structure of cross linkage of a three dimension in the molecular structure from an organic material.

[0022] Moreover, since the heat insulator of this invention according to claim 2 mixes the organic poly isocyanate and is characterized by carrying out reaction solidification, it can make the urethane aerogel grain

obtained in the molecular structure by drying the organogel constituent which has a urethane bond demonstrate effectively the heat insulation property of the aerogel which was excellent with few binders. Although the organic poly isocyanate which is a binder reacts with moisture, it becomes urethane resin and urethane aerogel grain is made to fix, it can paste up easily, and as for these of an ingredient of the same kind, bond strength is also high, and they can generate an insulator with rigidity.

•

[0023] Consequently, since the amount of binders can be controlled, the heat insulation property of the outstanding urethane aerogel grain becomes dominant. Moreover, since urethane aerogel itself has the bridge formation network structure as a description of an organic giant molecule, its rigidity is high and it has contributed to sharp reduction of the binder which is reinforcing materials.

[0024] Furthermore, since it consists of the urethane aerogel and the urethane resin binder of an ingredient of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it as an urethane material.

[0025] It is characterized by the thermal-protection-structure object indicated to claim 4 of this invention arranging said heat insulator between an inner plate and a shell plate, and really coming to foam on it from a rigid-urethane-foam raw material, said heat insulator is formed for the urethane material, and a thermal-protection-structure object with strong reinforcement with high bond strength is acquired for an ingredient of the same kind. Moreover, it can cast as a thermal-protection-structure object, without crushing aerogel by the blowing pressure force, even if it really foams by rigid urethane foam since the rigidity of the heat insulator obtained is high.

[0026] There is also no generating of the non-filling section from which inhibition of the restoration nature by collapse of the aerogel on the way of foaming becomes a cause especially, and high heat insulation property can be demonstrated as a thermal-protection-structure object. Furthermore, as a result of a thermal-protection-structure object's consisting of ingredients of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it.

[0027] After the thermal-protection-structure object indicated to claim 5 of this invention mixes the aerogel grain and the rigid-urethane-foam raw material which are obtained in the molecular structure by drying the organogel constituent which has a urethane bond, impregnation restoration is carried out between an inner plate and a shell plate, since it is the thermal-protection-structure object on which it really comes to foam, aerogel grain distributes to homogeneity in the heat insulation structure, and the homogeneous outstanding heat insulation property is obtained. Moreover, since it is formed for an urethane material of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it. In addition, a thermal-protection-structure object with strong reinforcement with high bond strength is acquired for an ingredient of the same kind.

[0028] Even when the thermal-protection-structure object indicated to claim 6 of this invention encloses with a nonwoven fabric the aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and arranges it between an inner plate and a shell plate and the heater section is near the insulated hot-water-storing container from heat-resistant height, there is no constraint of a covering surface product and it can be covered to near the heater section. Consequently, when it is used for an incubation hot-water-storing container like an electric water heater, it is possible to demonstrate the especially excellent heat insulation property.

[0029] It is the description that the thermal-protection-structure object indicated to claim 7 of this invention consists of said heat insulator and penetration objects, such as a nail, piping, and wiring, and the heat insulation property which excelled and was excellent in the design degree of freedom at the time of construction is demonstrated. In order that aerogel may demonstrate the heat insulation property which consisted of micropore below the average free degree of air, and was excellent in ordinary pressure, even if this has the exterior, a through hole, etc. in aerogel, heat insulation property does not change. For this reason, it has the outstanding heat insulation property, without spoiling the function of penetration objects, such as a nail, piping, and wiring. [0030] Hereafter, the gestalt of operation is explained using drawing 4 from drawing 1.

(Gestalt 1 of operation) When one example of the heat insulator 1 in the gestalt 1 of operation is explained using drawing 1, 2 is urethane aerogel and is granular aerogel which was made to carry out supercritical drying of the urethane gel which has a urethane bond, and obtained it. As an example which obtains urethane gel, to the polyether polyol 100 weight section of hydroxyl value 460 mgKOH/g, 1000 weight sections mixing of 2 weight sections and the acetone can be carried out [the polymeric MDI of the amine equivalent 135] for

KAOLIZER No.1 as the 115 weight sections and a catalyst, and urethane gel can be obtained as a resultant. [0031] Then, supercritical drying actuation by the carbon dioxide is performed, and the urethane aerogel which has nano order and which is overly a detailed porous body is obtained. This urethane aerogel is aerogel grain which consists of an organogel constituent of the mesh structure of cross linkage of a three dimension. [0032] 3 is a binder and a polymeric MDI and moisture consist the polymeric MDI of the amine equivalent 135 of a urethane resin constituent of the organic material which carried out reaction hardening by mixing to urethane aerogel at homogeneity in 5% and 2% of moisture. for promoting reaction hardening -- warming of 5kg/cm2 pressurization and 100-degreeC -- it can attain on conditions.

[0033] The thermal conductivity of the heat insulator at this time was 0.009 w/mK, the consistencies were 135 kg/m3 and 10% compressive strength was 78kPa.

[0034] Although BAIDA 3 has the binder function to paste up between urethane aerogel, since it consists of an urethane ingredient of the same kind, high bond strength is obtained and it can form a rigid high heat insulator. [0035] Consequently, since the amount of binders can be controlled, the heat insulation property of aerogel becomes dominant. Moreover, since urethane aerogel itself has the bridge formation network structure as a description of an organic giant molecule, its rigidity is high and it has contributed to sharp reduction of the binder which is reinforcing materials. Furthermore, since it consists of the urethane aerogel and the urethane resin binder of an ingredient of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it as an urethane material.

[0036] (Gestalt 2 of operation) The thermal-protection-structure object 4 of one example in the gestalt 2 of operation is shown in drawing 2. It consists of urethane aerogel and a binder and the space formed in a shell plate 5 and an inner plate 6 is made to arrange and pinch the heat insulator 1 which carried out hardening shaping. After having been filled up with the heat insulator 1 in the fixture which has the space beforehand formed with a shell plate 5 and an inner plate 6, solidifying it and attaching this in an inner plate 6, the thermalprotection-structure object 4 has been acquired by making a shell plate 5 meet a configuration and attaching it. [0037] Since a heat insulator 1 can be arranged without a clearance along the space formed in a shell plate 5 and an inner plate 6, it can demonstrate the heat insulation property which does not have heat leak, either and was excellent as a thermal-protection-structure object 4. Since especially the heat insulator 1 is obtained by mixed solidification of the organic poly isocyanate which are urethane aerogel grain and a binder, the shaping configuration does not have constraint and change, irregularity, etc. of thickness can design it freely. [0038] (Gestalt 3 of operation) The thermal-protection-structure object 7 of one example in the gestalt 3 of operation is shown in drawing 3. It consists of urethane aerogel and a binder and the heat insulator 1 which carried out hardening shaping is pasted up on the rear face of an inner plate 6, and a rigid-urethane-foam raw material is poured into the space formed with a shell plate 5, and it is really foaming to it. For this reason, the interior of the thermal-protection-structure object 7 except a heat insulator 1 is filled up with rigid urethane foam 8. such double layer structure -- a heat insulator 1 and rigid urethane foam 8 -- an ingredient of the same kind -- it is -- adhesion -- it was easy, and since the rigidity by foaming was really securable, there was no deformation of the thermal-protection-structure object 7.

[0039] (Gestalt 4 of operation) The thermal-protection-structure object 9 of one example in the gestalt 4 of operation is shown in <u>drawing 4</u>. The urethane aerogel grain 2 and a rigid-urethane-foam raw material are mixed, between a shell plate 5 and an inner plate 6, impregnation restoration is carried out and the thermal-protection-structure object 9 is formed. A mixed weight ratio is 3:7 and is distributed to homogeneity in rigid urethane foam 8.

[0040] Consequently, aerogel grain can be arranged also in the part which cannot arrange said heat insulators 1, such as pars convolute lobuli corticalis renis, and heat insulation property can be strengthened as a whole. furthermore, a heat insulator 1 and rigid urethane foam 8 -- an ingredient of the same kind -- it is -- adhesion -- since it was easy, and interlaminar peeling did not happen but rigidity was secured, even if it used the reinforcement of the thermal-protection-structure object 7 as an adiabatic wall for refrigeration practically satisfactory, there was no deformation of curvature etc.

[0041] (Gestalt 5 of operation) The thermal-protection-structure object 10 of one example in the gestalt 5 of operation is shown in <u>drawing 5</u>. The thermal-protection-structure object 10 consists of the heater sections 14 with which an outer container 11, the contents machine 12, and the contents machine lower part 13 were equipped. Water is poured into the contents machine 12 in water, water can be boiled with heating of the heater section 14, and hot water storing is carried out. Between an outer container 11 and the contents machine 12, the

nonwoven fabric 15 which consists of a glass fiber which packed the urethane aerogel grain 2 is arranged. [0042] The nonwoven fabric 15 is covered to the contents machine lower part 13 which touches the heater section which reaches 170-degreeC. Consequently, the jacket was carried out with the film-like plastics container, rather than the vacuum insulation material which cannot cover the contents machine lower part 13 from the problem of the dissolution, about 25% of coverage improved and heat retention has improved 20% by consumed-electric-power conversion.

[0043] (Gestalt 6 of operation) The thermal-protection-structure object 15 of one example in the gestalt 6 of operation is shown in <u>drawing 6</u>. The thermal-protection-structure object 15 processes the through hole 16 for piping installation into the thermal-protection-structure object 4. Although the penetration objects 17, such as refrigerant piping, were arranged in the through hole 16, construction also showed after this that the heat insulation property of the thermal-protection-structure object 15 had the outstanding heat insulation property not changeful. When vacuum insulation material is arranged instead of a heat insulator 1 and same post-construction was performed as a comparison, heat insulation property deteriorated to one fifth, and the role exertion of it as a heat insulator was not completed.

[Effect of the Invention] So that clearly from the place described above invention according to claim 1 While making the aerogel grain which consists of an organogel constituent which has the mesh structure of cross linkage of a three dimension in the molecular structure react with the binder which consists of an organic material, invention according to claim 2 To the urethane aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond Since it is the heat insulator which mixed the organic poly isocyanate and was characterized by carrying out reaction solidification, the heat insulation property of aerogel excellent in few binders can be demonstrated effectively.

[0045] Although the organic poly isocyanate which is a binder reacts with moisture, it becomes urethane resin and urethane aerogel grain is made to fix, it can paste up easily, and as for these of an ingredient of the same kind, bond strength is also high, and they can generate an insulator with rigidity. Consequently, since the amount of binders can be controlled, the heat insulation property of the outstanding urethane aerogel grain becomes dominant.

[0046] Moreover, since urethane aerogel itself has the bridge formation network structure as a description of an organic giant molecule, its rigidity is high and it has contributed to sharp reduction of the binder which is reinforcing materials.

[0047] Furthermore, since it consists of the urethane aerogel and the urethane resin binder of an ingredient of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it as an urethane material.

[0048] Invention of claim 4 arranges said heat insulator between an inner plate and a shell plate, since it is the thermal-protection-structure object on which it really comes to foam from a rigid-urethane-foam raw material, said heat insulator is formed for the urethane material, and a thermal-protection-structure object with strong reinforcement with high bond strength is acquired for an ingredient of the same kind. Moreover, it can cast as a thermal-protection-structure object, without crushing aerogel by the blowing pressure force, even if it rigid urethane foam and really foams since the rigidity of the heat insulator obtained is high.

[0049] There is also no generating of the non-filling section from which inhibition of the restoration nature by collapse of the aerogel on the way of foaming becomes a cause especially, and high heat insulation property can be demonstrated as a thermal-protection-structure object.

[0050] Furthermore, as a result of a thermal-protection-structure object's consisting of ingredients of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it.

[0051] After mixing the aerogel grain and the rigid-urethane-foam raw material which are obtained by invention of claim 5 drying the organogel constituent which has a urethane bond in the molecular structure, impregnation restoration is carried out between an inner plate and a shell plate, since it is the thermal-protection-structure object on which it really comes to foam, aerogel grain distributes to homogeneity in the heat insulation structure, and the homogeneous outstanding heat insulation property is obtained.

[0052] Moreover, since it is formed for an urethane material of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it. In addition, a thermal-protection-structure object with strong reinforcement with high bond strength is acquired for an ingredient of

the same kind.

[0053] Invention of claim 6 encloses with a nonwoven fabric the aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and from heat-resistant height, since it is the thermal-protection-structure object arranged between the inner plate and the shell plate, even when the heater section is near the insulated hot-water-storing container, there is no constraint of a covering surface product and it can be covered to near the heater section.

[0054] Consequently, when it is used for an incubation hot-water-storing container like the electric water heater which employed the description of the high urethane aerogel of heat-resistant ability efficiently, it is possible to demonstrate the especially excellent heat insulation property.

[0055] Invention of claim 7 is a thermal-protection-structure object which consists of said heat insulator and penetration objects, such as a nail, piping, and wiring, and the heat insulation property which excelled and was excellent in the design degree of freedom at the time of construction is demonstrated.

[0056] In order that aerogel may demonstrate the heat insulation property which consisted of micropore below the average free degree of air, and was excellent in ordinary pressure, even if this has the exterior, a through hole, etc. in aerogel, heat insulation property does not change.

[0057] For this reason, it has the outstanding heat insulation property, without spoiling the function of penetration objects, such as a nail, piping, and wiring.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the thermal-protection-structure object which comes to arrange the heat insulator used for a residence, an incubation heat insulation device, etc., and a heat insulator.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] In recent years, high performance-ization of a heat insulator serves as a very important theme from a viewpoint of energy saving. Especially, by the residence or the incubation heat insulation device, efficient use of the heat energy by heat insulation occupies the big ratio in energy saving, and various measures are made to the improvement in heat insulation property of the heat insulator to constitute. [0003] In order to acquire the large energy-saving effectiveness especially, the attempt which is going to obtain the engine performance beyond twice is also made to the heat insulation property of the rigid urethane foam in the level which was excellent as a general-purpose heat insulator. They are the vacuum insulation material which decompressed the interior and specifically controlled the effect of gas heat conduction sharply, and the aerogel heat insulator with which it micropore-ized to the distance between openings below the average free process of air, and ordinary pressure also reduced gas thermal conductivity sharply.

[0004] For example, about vacuum insulation material, the core material which consists of detailed inorganic powder tends to be housed with a film-like plastic envelope, reduced pressure closure of the interior tends to be carried out at 1mmHg, and it is going to improve to about 2 times [of rigid urethane foam] heat insulation property by effect reduction of gas heat conduction as shown in JP,2-33917,B.

[0005] Moreover, an aerogel heat insulator includes silica aerogel with a binder, as shown in an EP-A -340707 [No.] official report, and it has the distance between openings below the gas mean free path of air, and the heat insulator which reduced gas thermal conductivity sharply is proposed.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] It is invention according to claim 1 so that clearly from the place described above, Since it is the heat insulator characterized by for invention according to claim 2 having mixed the organic poly isocyanate to the urethane aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and carrying out reaction solidification while making the aerogel grain which consists of an organogel constituent which has the mesh structure of cross linkage of a three dimension in the molecular structure react with the binder which consists of an organic material, the heat insulation property of aerogel excellent in few binders can be demonstrated effectively.

[0045] Although the organic poly isocyanate which is a binder reacts with moisture, it becomes urethane resin and urethane aerogel grain is made to fix, it can paste up easily, and as for these of an ingredient of the same kind, bond strength is also high, and they can generate an insulator with rigidity. Consequently, since the amount of binders can be controlled, the heat insulation property of the outstanding urethane aerogel grain becomes dominant.

[0046] Moreover, since urethane aerogel itself has the bridge formation network structure as a description of an organic giant molecule, its rigidity is high and it has contributed to sharp reduction of the binder which is reinforcing materials.

[0047] Furthermore, since it consists of the urethane aerogel and the urethane resin binder of an ingredient of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it as an urethane material.

[0048] Invention of claim 4 arranges said heat insulator between an inner plate and a shell plate, since it is the thermal-protection-structure object on which it really comes to foam from a rigid-urethane-foam raw material, said heat insulator is formed for the urethane material, and a thermal-protection-structure object with strong reinforcement with high bond strength is acquired for an ingredient of the same kind. Moreover, it can cast as a thermal-protection-structure object, without crushing aerogel by the blowing pressure force, even if it rigid urethane foam and really foams since the rigidity of the heat insulator obtained is high.

[0049] There is also no generating of the non-filling section from which inhibition of the restoration nature by collapse of the aerogel on the way of foaming becomes a cause especially, and high heat insulation property can be demonstrated as a thermal-protection-structure object.

[0050] Furthermore, as a result of a thermal-protection-structure object's consisting of ingredients of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it.

[0051] After mixing the aerogel grain and the rigid-urethane-foam raw material which are obtained by invention of claim 5 drying the organogel constituent which has a urethane bond in the molecular structure, impregnation restoration is carried out between an inner plate and a shell plate, since it is the thermal-protection-structure object on which it really comes to foam, aerogel grain distributes to homogeneity in the heat insulation structure, and the homogeneous outstanding heat insulation property is obtained.

[0052] Moreover, since it is formed for an urethane material of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it. In addition, a thermalprotection-structure object with strong reinforcement with high bond strength is acquired for an ingredient of the same kind.

[0053] Invention of claim 6 encloses with a nonwoven fabric the aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and from heat-resistant height, since it is the thermal-protection-structure object arranged between the inner plate and the shell plate, even when the

heater section is near the insulated hot-water-storing container, there is no constraint of a covering surface product and it can be covered to near the heater section.

[0054] Consequently, when it is used for an incubation hot-water-storing container like the electric water heater which employed the description of the high urethane aerogel of heat-resistant ability efficiently, it is possible to demonstrate the especially excellent heat insulation property.

[0055] Invention of claim 7 is a thermal-protection-structure object which consists of said heat insulator and penetration objects, such as a nail, piping, and wiring, and the heat insulation property which excelled and was excellent in the design degree of freedom at the time of construction is demonstrated.

[0056] In order that aerogel may demonstrate the heat insulation property which consisted of micropore below the average free degree of air, and was excellent in ordinary pressure, even if this has the exterior, a through hole, etc. in aerogel, heat insulation property does not change.

[0057] For this reason, it has the outstanding heat insulation property, without spoiling the function of penetration objects, such as a nail, piping, and wiring.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] In vacuum insulation material, it cannot be overemphasized that it is required in the improvement in heat insulation property to carry out reduced pressure maintenance of the interior as JP,2-33917,B is shown. since [however,] jacket material consists of plastic envelopes -- heat -- getting damaged -- bag tearing might be carried out, like the electric water heater which is an incubation device, the nail was struck after use near the heater, or construction, and there was many accident from which a vacuum break arises by laminate film penetration in the example used as a heat insulator for residences with which post-construction of letting piping pass is added. Thus, in order to apply a heat insulator broadly industrially, the high performance heat insulator which can be equal to various construction from a viewpoint of dependability is indispensable.

[0007] On the other hand, since inorganic silica aerogel is used and there is no mesh structure of cross linkage of a three dimension into the molecular structure fundamentally in aerogel although binder content is made below into 50% volume for utilizing the engine performance of aerogel, and reservation on the strength as shown by the EP-A -340707 [No.] official report, it is difficult for there to be no rigidity and to reduce a binder sharply substantially. For this reason, there is a problem from which only about the same heat insulation property as glass wool is obtained in response to the bad influence of a binder.

[0008] Even if it penetrates, it offers a heat insulator and a thermal-protection-structure object excellent in practical use workability without performance degradation, while reservation on the strength can do this invention and it can demonstrate the heat insulation property of about the same high performance as vacuum insulation material in view of the above-mentioned technical problem, even if binder content is small.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] In order to attain this purpose, this invention is considered as the following configurations.

[0010] Since the heat insulator concerning claim 1 of this invention carries out reaction solidification of the aerogel grain which consists of an organogel constituent which has the mesh structure of cross linkage of a three dimension in the molecular structure with the binder which consists of an organic material, and the high organogel constituent of crosslinking density is used, rigidity becomes high.

[0011] The heat insulator concerning claim 2 of this invention mixes the organic poly isocyanate to the urethane aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond as a binder, and it is made to solidify it.

[0012] Since rigidity becomes high by using the urethane aerogel which has the high urethane bond of crosslinking density according to this invention, the binder which is reinforcing materials can be reduced sharply, the heat insulation property which was excellent in urethane aerogel grain as a result becomes dominant, and the heat insulator of high performance is obtained.

[0013] Moreover, the thermal-protection-structure object concerning claim 4 of this invention arranges said heat insulator in the interior of the structure which consists of an inner plate and a shell plate, and it really comes to foam on it from a rigid-urethane-foam raw material.

[0014] It can cast as a thermal-protection-structure object, without crushing aerogel by the blowing pressure force, even if it really foams by rigid urethane foam since the rigidity of said heat insulator obtained is high according to this invention. There is also no generating of the non-filling section from which inhibition of the restoration nature by collapse of the aerogel on the way of foaming becomes a cause especially, and high heat insulation property can be demonstrated as a thermal-protection-structure object.

[0015] Moreover, after the thermal-protection-structure object concerning claim 5 of this invention mixes the aerogel grain and the rigid-urethane-foam raw material which are obtained in the molecular structure by drying the organogel constituent which has a urethane bond, it carries out impregnation restoration and really comes to foam between an inner plate and a shell plate.

[0016] Since homogeneity can be made to distribute the aerogel which has the outstanding heat insulation property in the heat insulation structure according to this invention, the outstanding heat insulation property can contribute to the whole thermal-protection-structure object.

[0017] Moreover, the thermal-protection-structure object concerning claim 6 of this invention encloses with a nonwoven fabric the aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and is characterized by arranging between an inner plate and a shell plate.

[0018] According to this invention, since the rigidity of aerogel is high and it is not crushed by vibration etc., it is usable as a heat insulation member at configuration maintenance of extent put into a nonwoven fabric. Moreover, from heat-resistant height, even when the heater section is near the insulated hot-water-storing container, there is no constraint of a covering surface product and it can be covered to near the heater section. Consequently, when it is used for an incubation hot-water-storing container like an electric water heater, it is possible to demonstrate the outstanding heat insulation property by high coverage, and it can contribute to energy saving.

[0019] Moreover, the thermal-protection-structure object concerning claim 7 of this invention is characterized by penetration objects, such as a nail, piping, and wiring, being arranged by the thermal-protection-structure object.

[0020] According to this invention, aerogel consists of micropore below the average free degree of air, and in

order to demonstrate the heat insulation property excellent in ordinary pressure, even if the exterior, a through hole, etc. are in aerogel, heat insulation property does not change. For this reason, it has the outstanding heat insulation property, without spoiling the function of penetration objects, such as a nail, piping, and wiring. [0021]

[Embodiment of the Invention] Reaction solidification of the heat insulator of this invention according to claim 1 is carried out with the binder which becomes the aerogel grain which consists of an organogel constituent which has the mesh structure of cross linkage of a three dimension in the molecular structure from an organic material.

[0022] Moreover, since the heat insulator of this invention according to claim 2 mixes the organic poly isocyanate and is characterized by carrying out reaction solidification, it can make the urethane aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond demonstrate effectively the heat insulation property of the aerogel which was excellent with few binders. Although the organic poly isocyanate which is a binder reacts with moisture, it becomes urethane resin and urethane aerogel grain is made to fix, it can paste up easily, and as for these of an ingredient of the same kind, bond strength is also high, and they can generate an insulator with rigidity.

[0023] Consequently, since the amount of binders can be controlled, the heat insulation property of the outstanding urethane aerogel grain becomes dominant. Moreover, since urethane aerogel itself has the bridge formation network structure as a description of an organic giant molecule, its rigidity is high and it has contributed to sharp reduction of the binder which is reinforcing materials.

[0024] Furthermore, since it consists of the urethane aerogel and the urethane resin binder of an ingredient of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it as an urethane material.

[0025] It is characterized by the thermal-protection-structure object indicated to claim 4 of this invention arranging said heat insulator between an inner plate and a shell plate, and really coming to foam on it from a rigid-urethane-foam raw material, said heat insulator is formed for the urethane material, and a thermal-protection-structure object with strong reinforcement with high bond strength is acquired for an ingredient of the same kind. Moreover, it can cast as a thermal-protection-structure object, without crushing aerogel by the blowing pressure force, even if it really foams by rigid urethane foam since the rigidity of the heat insulator obtained is high.

[0026] There is also no generating of the non-filling section from which inhibition of the restoration nature by collapse of the aerogel on the way of foaming becomes a cause especially, and high heat insulation property can be demonstrated as a thermal-protection-structure object. Furthermore, as a result of a thermal-protection-structure object's consisting of ingredients of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it.

[0027] After the thermal-protection-structure object indicated to claim 5 of this invention mixes the aerogel grain and the rigid-urethane-foam raw material which are obtained in the molecular structure by drying the organogel constituent which has a urethane bond, impregnation restoration is carried out between an inner plate and a shell plate, since it is the thermal-protection-structure object on which it really comes to foam, aerogel grain distributes to homogeneity in the heat insulation structure, and the homogeneous outstanding heat insulation property is obtained. Moreover, since it is formed for an urethane material of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it. In addition, a thermal-protection-structure object with strong reinforcement with high bond strength is acquired for an ingredient of the same kind.

[0028] Even when the thermal-protection-structure object indicated to claim 6 of this invention encloses with a nonwoven fabric the aerogel grain obtained in the molecular structure by drying the organogel constituent which has a urethane bond, and arranges it between an inner plate and a shell plate and the heater section is near the insulated hot-water-storing container from heat-resistant height, there is no constraint of a covering surface product and it can be covered to near the heater section. Consequently, when it is used for an incubation hot-water-storing container like an electric water heater, it is possible to demonstrate the especially excellent heat insulation property.

[0029] It is the description that the thermal-protection-structure object indicated to claim 7 of this invention consists of said heat insulator and penetration objects, such as a nail, piping, and wiring, and the heat insulation property which excelled and was excellent in the design degree of freedom at the time of construction is

demonstrated. In order that aerogel may demonstrate the heat insulation property which consisted of micropore below the average free degree of air, and was excellent in ordinary pressure, even if this has the exterior, a through hole, etc. in aerogel, heat insulation property does not change. For this reason, it has the outstanding heat insulation property, without spoiling the function of penetration objects, such as a nail, piping, and wiring. [0030] Hereafter, the gestalt of operation is explained using drawing 4 from drawing 1.

(Gestalt 1 of operation) When one example of the heat insulator 1 in the gestalt 1 of operation is explained using drawing 1, 2 is urethane aerogel and is granular aerogel which was made to carry out supercritical drying of the urethane gel which has a urethane bond, and obtained it. As an example which obtains urethane gel, to the polyether polyol 100 weight section of hydroxyl value 460 mgKOH/g, 1000 weight sections mixing of 2 weight sections and the acetone can be carried out [the polymeric MDI of the amine equivalent 135] for KAOLIZER No.1 as the 115 weight sections and a catalyst, and urethane gel can be obtained as a resultant. [0031] Then, supercritical drying actuation by the carbon dioxide is performed, and the urethane aerogel which has nano order and which is overly a detailed porous body is obtained. This urethane aerogel is aerogel grain which consists of an organogel constituent of the mesh structure of cross linkage of a three dimension. [0032] 3 is a binder and a polymeric MDI and moisture consist the polymeric MDI of the amine equivalent 135 of a urethane resin constituent of the organic material which carried out reaction hardening by mixing to urethane aerogel at homogeneity in 5% and 2% of moisture. for promoting reaction hardening -- warming of 5kg/cm2 pressurization and 100-degreeC -- it can attain on conditions.

[0033] The thermal conductivity of the heat insulator at this time was 0.009 w/mK, the consistencies were 135 kg/m3 and 10% compressive strength was 78kPa.

[0034] Although BAIDA 3 has the binder function to paste up between urethane aerogel, since it consists of an urethane ingredient of the same kind, high bond strength is obtained and it can form a rigid high heat insulator. [0035] Consequently, since the amount of binders can be controlled, the heat insulation property of aerogel becomes dominant. Moreover, since urethane aerogel itself has the bridge formation network structure as a description of an organic giant molecule, its rigidity is high and it has contributed to sharp reduction of the binder which is reinforcing materials. Furthermore, since it consists of the urethane aerogel and the urethane resin binder of an ingredient of the same kind, the collection at the time of member disposal by type is unnecessary, and recycle-izing is easily possible for it as an urethane material.

[0036] (Gestalt 2 of operation) The thermal-protection-structure object 4 of one example in the gestalt 2 of operation is shown in drawing 2. It consists of urethane aerogel and a binder and the space formed in a shell plate 5 and an inner plate 6 is made to arrange and pinch the heat insulator 1 which carried out hardening shaping. After having been filled up with the heat insulator 1 in the fixture which has the space beforehand formed with a shell plate 5 and an inner plate 6, solidifying it and attaching this in an inner plate 6, the thermalprotection-structure object 4 has been acquired by making a shell plate 5 meet a configuration and attaching it. [0037] Since a heat insulator 1 can be arranged without a clearance along the space formed in a shell plate 5 and an inner plate 6, it can demonstrate the heat insulation property which does not have heat leak, either and was excellent as a thermal-protection-structure object 4. Since especially the heat insulator 1 is obtained by mixed solidification of the organic poly isocyanate which are urethane aerogel grain and a binder, the shaping configuration does not have constraint and change, irregularity, etc. of thickness can design it freely. [0038] (Gestalt 3 of operation) The thermal-protection-structure object 7 of one example in the gestalt 3 of operation is shown in drawing 3. It consists of urethane aerogel and a binder and the heat insulator 1 which carried out hardening shaping is pasted up on the rear face of an inner plate 6, and a rigid-urethane-foam raw material is poured into the space formed with a shell plate 5, and it is really foaming to it. For this reason, the interior of the thermal-protection-structure object 7 except a heat insulator 1 is filled up with rigid urethane foam 8. such double layer structure -- a heat insulator 1 and rigid urethane foam 8 -- an ingredient of the same kind -- it is -- adhesion -- it was easy, and since the rigidity by foaming was really securable, there was no deformation of the thermal-protection-structure object 7.

[0039] (Gestalt 4 of operation) The thermal-protection-structure object 9 of one example in the gestalt 4 of operation is shown in drawing 4. The urethane aerogel grain 2 and a rigid-urethane-foam raw material are mixed, between a shell plate 5 and an inner plate 6, impregnation restoration is carried out and the thermal-protection-structure object 9 is formed. A mixed weight ratio is 3:7 and is distributed to homogeneity in rigid urethane foam 8.

[0040] Consequently, aerogel grain can be arranged also in the part which cannot arrange said heat insulators 1,

such as pars convoluta lobuli corticalis renis, and heat insulation property can be strengthened as a whole. furthermore, a heat insulator 1 and rigid urethane foam 8 -- an ingredient of the same kind -- it is -- adhesion -- since it was easy, and interlaminar peeling did not happen but rigidity was secured, even if it used the reinforcement of the thermal-protection-structure object 7 as an adiabatic wall for refrigeration practically satisfactory, there was no deformation of curvature etc.

[0041] (Gestalt 5 of operation) The thermal-protection-structure object 10 of one example in the gestalt 5 of operation is shown in drawing 5. The thermal-protection-structure object 10 consists of the heater sections 14 with which an outer container 11, the contents machine 12, and the contents machine lower part 13 were equipped. Water is poured into the contents machine 12 in water, water can be boiled with heating of the heater section 14, and hot water storing is carried out. Between an outer container 11 and the contents machine 12, the nonwoven fabric 15 which consists of a glass fiber which packed the urethane aerogel grain 2 is arranged. [0042] The nonwoven fabric 15 is covered to the contents machine lower part 13 which touches the heater section which reaches 170-degreeC. Consequently, the jacket was carried out with the film-like plastics container, rather than the vacuum insulation material which cannot cover the contents machine lower part 13 from the problem of the dissolution, about 25% of coverage improved and heat retention has improved 20% by consumed-electric-power conversion.

[0043] (Gestalt 6 of operation) The thermal-protection-structure object 15 of one example in the gestalt 6 of operation is shown in <u>drawing 6</u>. The thermal-protection-structure object 15 processes the through hole 16 for piping installation into the thermal-protection-structure object 4. Although the penetration objects 17, such as refrigerant piping, were arranged in the through hole 16, construction also showed after this that the heat insulation property of the thermal-protection-structure object 15 had the outstanding heat insulation property not changeful. When vacuum insulation material is arranged instead of a heat insulator 1 and same post-construction was performed as a comparison, heat insulation property deteriorated to one fifth, and the role exertion of it as a heat insulator was not completed.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The mimetic diagram of the heat insulator in the operation gestalt 1 of this invention

Drawing 2] The mimetic diagram of the thermal-protection-structure object in the operation gestalt 2 of this invention

[Drawing 3] The mimetic diagram of the thermal-protection-structure object in the operation gestalt 3 of this invention

[Drawing 4] The mimetic diagram of the thermal-protection-structure object in the operation gestalt 4 of this invention

[Drawing 5] The mimetic diagram of the thermal-protection-structure object in the operation gestalt 5 of this invention

[Drawing 6] The mimetic diagram of the thermal-protection-structure object in the operation gestalt 6 of this invention

[Description of Notations]

- 1. Heat Insulator
- 2. Urethane Aerogel Grain
- 3. Binder
- 4.7.9.10.15. Thermal-Protection-Structure Object
- 5. Shell Plate
- 6. Inner Plate
- 15. Nonwoven Fabric

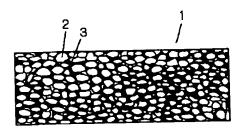
JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

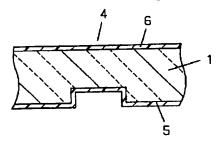
- 1 断熱材
- 2 ウレタンエアロゲル粒体
- 3 パインダー



[Drawing 2]

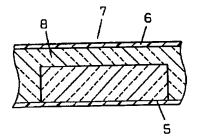
4 断熱構造体 5 外板

6 内板

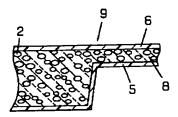


[Drawing 3]

7 断熱構造体 8 硬質ウレタンフォーム

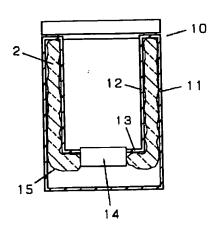


[Drawing 4]



[Drawing 5]

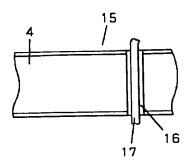
10 断熱構造体 15 不錄布



[Drawing 6]

5 断熱構造体

17 貫通物



PAT-NO: JP02001082682A

DOCUMENT-IDENTIFIER: JP 2001082682 A

TITLE: HEAT INSULATING MATERIAL AND HEAT INSULATING STRUCTURE

PUBN-DATE: March 30, 2001

INVENTOR-INFORMATION:

NAME
UEKADO, KAZUTO

COUNTRY
N/A

ASSIGNEE-INFORMATION:

NAME
MATSUSHITA REFRIG CO LTD

COUNTRY
N/A

APPL-NO: JP11257041

APPL-DATE: September 10, 1999

INT-CL (IPC): F16L059/02, C08G018/40 , C08J009/00

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a heat insulating material and a heat insulating structure capable of securing strength even when binder content is small, displaying heat insulating performance of high performance as a vacuum heat insulating material, preventing deterioration of performance even when it is perforated and excellent in practical workability.

SOLUTION: It is possible to provide a heat insulating material 1 of high performance as a binder 3 which is a reinforcing material can be reduced and as a result, an excellent heat insulating characteristic of a urethane aero gel granular body 2 becomes dominant as rigidity is impoved by using a urethane aero gel having high bridged density urethane bonding with the urethane aero gel granular body 2 mixed and solidified with organic polyisosianate as the binder 3.

COPYRIGHT: (C)2001,JPO

(19)日本国特許庁(JP)

(12) 公開特許公報(A)

(11)特許出願公閱番号 特開2001-82682 (P2001-82682A)

(43)公開日 平成13年3月30日(2001.3.30)

| | and the second s | FI | テーマコード(多考) |
|---------------|--|---------------|-------------------------|
| (51) Int.Cl.' | 識別記号 | • • | 3H036 |
| F16L 59/02 | | F16L 59/02 | |
| | | C 0 8 G 18/40 | 4F074 |
| C 0 8 G 18/40 | | C08J 9/00 | CFF 4J034 |
| COSI 9/00 | CFF | C081 3/00 | |

審査請求 未請求 請求項の数? OL (全 7 頁)

| (21)出顯書号 | 特顏平 11-257041 | (71)出國人 | 000004488 松下冷機株式会社 | |
|----------|-----------------------|---------|--|--|
| (22)出顧日 | 平成11年9月10日(1999.9.10) | (72)発明者 | 大阪府東大阪市高井田本通4丁目2番5号 上門 一登 大阪府東大阪市高井田本通4丁目2番5号 松下冷橋株式会社内 | |
| | | (74)代理人 | 100097445 弁理士 岩橋 文雄 (外2名) | |

最終頁に抜く

(54) 【発明の名称】 断熱材及び新熱構造体

(57)【要約】

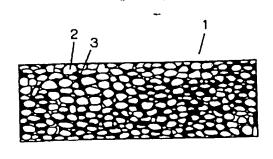
【課題】 バインダー含有率が小さくても強度確保ができ、真空断熱材並の高性能の断熱性能を発揮できると共に、貫通しても性能劣化がない実用加工性に優れた断熱材と断熱構造体を提供する。

【解決手段】 ウレタンエアロゲル粒体 2にバインダー 3として有機ポリイソシアネートを混合し固化させたもので、架橋密度の高いウレタン結合を有するウレタンエアロゲルを用いることで、開性が高くなるため、補強材であるバインダー3を低減でき、結果としてウレタンエアロゲル粒体 2の優れた断熱特性が支配的となり、高性能の断熱材1が得られる。

1 断熱材

2 ウレタンエアロゲル粒体

3 パインダー



【特許請求の範囲】

【請求項1】 分子構造中に3次元の網目架橋構造を有 する有機ゲル組成物からなるエアロゲル粒体を、有機材 料からなるバインダーで反応固化させたことを特徴とす る断無材。

l

【請求項2】 分子構造中にウレタン結合を有する有機 ゲル組成物を乾燥して得られるエアロゲル粒体に、バイ ンダーとして有機ポリイソシアネートを混合し、反応固 化させたことを特徴とする断熱材。

【請求項3】 有機ポリイソシアネートをエアロゲル粒 10 体に対して2~15%混合させてなる請求項2記載の断 熟材。

【請求項4】 内板と外板との間に、分子構造中にウレ タン結合を有する有機ゲル組成物を乾燥して得られるエ アロゲル粒体にバインダーとして 有機ポリイソシアネ ートを混合し反応固化させた断熱材を配設し、前記両板 間に硬質ウレタンフォームを一体発泡してなる断熱構造 休.

【請求項5】 分子構造中にウレタン結合を有する有機 ゲル組成物を乾燥して得られるエアロゲル粒体と硬質ウ 20 レタンフォーム原料を混合した後、内板と外板間に充填 したことを特徴とする断熱構造体。

【請求項6】 内板と外板との間に、分子構造中にウレ タン結合を有する有機ゲル組成物を乾燥して得られる工 アロゲル粒体を不識布に封入して配設したことを特徴と する断熱構造体。

【請求項7】 釘、配管、配線などの貫通物を備えた請 求項4から6のいずれか一項記載の断熱構造体。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は、住宅や保温保冷機 器等に用いる断熱材と、断熱材を配設してなる断熱構造 体に関するものである。

[0002]

【従来の技術】近年、省エネルギーの観点から断熱材の 高性能化が極めて重要なテーマとなっている。特に住宅 や保温保冷機器等では、断熱による熱エネルギーの効率 的な利用が、省エネルギーにおいて大きな比率を占めて おり、構成する断熱材の断熱性能向上に対して様々な取 り組みがなされている。

【0003】特に、大幅な省エネルギー効果を得るた め、汎用断熱材として優れたレベルにある硬質ウレタン フォームの断熱性能に対して、倍以上の性能を得ようと する試みもなされている。具体的には、内部を減圧して 気体熱伝導の影響を大幅に抑制した真空断熱材や、空気 の平均自由工程以下の空隙間距離まで微細孔化し、常圧 でも気体熱伝導率を大幅に低減したエアロゲル断熱材で ある。

【0004】例えば、真空断熱材については、特公平2 -33917号公報に示されているように、微細無機粉 50

木からなる芯材をフィルム状プラスチック容器で外被 し、内部を1mmlgに減圧封止するもので、気体熱伝 導の影響低減により、硬質ウレタンフォームの2倍程度 の断熱性能に改善しようとするものである。

2

【0005】また、エアロゲル断熱材は、EP-A-3 40707号公報に示されるようにシリカエアロゲルを 結合剤で包含し、空気の気体平均自由行程以下の空隙間 距離を有し、気体熱伝導率を大幅に低減した断熱材が提 案されている。

[0006]

【発明が解決しようとする課題】真空断熱材において は、特公平2-33917号公報において示されるよう に内部を減圧維持することが断熱性能向上において必要 であることはいうまでもない。しかしながら、外被材が プラスチック容器で構成されているため、熱と傷つきに よって破袋する可能性があり、保温機器である電気温水 器のようにヒータ近傍での使用や施工後に釘を打った り、配管を通す等の後工事が加わるような住宅用断熱材 として使用する事例では、ラミネートフィルム貫通によ り、真空破壊が起こる事故が多くあった。このように工 業的に幅広く断熱材を適用するには、信頼性という観点 から、種々の施工に耐えられる高性能断熱材が不可欠で

【0007】一方、エアロゲルにおいては、EP-A-340707号公報で示されるように、エアロゲルの性 能を活かすことと強度確保のために、バインダー含有率 を50%体積以下としているが、無機のシリカエアロゲ ルを使用しているため、基本的に分子構造中に3次元の 網目架橋構造がないため、剛性がなく、実質的にバイン 30 ダーを大幅に減らすことは困難である。このため、バイ ンダーの悪影響を受けてグラスウール並の断熱性能しか 得られない問題がある。

【0008】本発明は、上記課題に鑑み、バインダー含 有率が小さくても強度確保ができ、真空断熱材並の高性 能の断熱性能を発揮できると共に、貫通しても性能劣化 がない実用加工性に優れた断熱材と断熱構造体を提供す るものである。

100091

【課題を解決するための手段】この目的を達成するた 40 め、本発明は以下のような構成とする。

【0010】本発明の請求項1に係る断熱材は、分子構 造中に3次元の網目架橋構造を有する有機ゲル組成物か らなるエアロゲル拉体を有機材料からなるバインダーで 反応固化させているので、架橋密度の高い有機ゲル組成 物を用いるので剛性が高くなる。

【0011】本発明の請求項2に係る断無材は、分子構 造中にウレタン結合を有する有機ゲル組成物を乾燥して 得られるウレタンエアロゲル粒体にバインダーとして有 機ポリイソシアネートを混合し、固化させたものであ

【0012】本発明によれば、架橋密度の高いウレタン 結合を有するウレタンエアロゲルを用いることで、剛性 が高くなるため、補強材であるバインダーを大幅に低減 でき、結果としてウレタンエアロゲル粒体の優れた断熱 特性が支配的となり、高性能の断熱材が得られるのであ る.

【0013】また、本発明の請求項4に係る断熱構造体 は、内坂と外板とで構成される構造体内部に前記断熱材 を配設し、硬質ウレタンフォーム原料で一体発泡してな るものである。

【0014】本発明によれば、得られる前記断熱材の剛 性が高いため、硬質ウレタンフォームで一体発泡しても 発泡圧力でエアロゲルがつぶれることもなく、断熱構造 体として成型できる。特に、発泡途上でのエアロゲルの 崩壊による充填性の阻害が原因となる未充填部の発生も なく、断熱構造体として高断熱性能が発揮できるのであ る.

【0015】また、本発明の請求項5に係る断熱構造体 は、分子構造中にウレタン結合を有する有機ゲル組成物 を乾燥して得られるエアロゲル粒体と硬質ウレタンフォ 20 ーム原料を混合した後、内板と外板間に注入充填し、一 体発泡してなるものである。

【0016】木発明によれば、優れた断熱性能を有する エアロゲルを均一に断熱構造体中に分散させることがで きるため、優れた断熱性能が断熱構造体全体に寄与する ことができる。

【0017】また、本発明の請求項6に係る断熱構造体 は、分子構造中にウレタン結合を有する有機ゲル組成物 を乾燥して得られるエアロゲル粒体を不識布に封入し、 内板と外板間に配設したことを特徴とするものである。 【0018】本発明によれば、エアロゲルの剛性が高い ため、振動等によってつぶれることがないため、不識布 に入れる程度の形状保持で断熱部材として使用可能であ る。また、耐熱性の高さから、ヒーター部が被断熱貯湯 容器の近傍にあるような場合でも、被覆面積の制約はな く、ヒーター部の近傍まで被覆することができる。この 結果、電気温水器のような保温貯湯容器に使用した場 合、優れた断熱性能を高い被覆率で発揮することが可能 であり、省エネルギーに寄与できるのである。

【0019】また、本発明の請求項7に係る断熱構造体 は、断熱構造体に釘、配管、配線などの貫通物が配設さ れたことを特徴とするものである。

【0020】本発明によれば、エアロゲルは空気の平均 自由程以下の微細孔からなり、常圧で優れた断熱性能を 発揮するため、エアロゲル内に外部と貫通穴などがあっ たとしても断熱性能は変化しない。このため、釘、配 管、配線などの貫通物の機能を損なうことなく、優れた 断熱性能を有するのである。

[0021]

は、分子構造中に3次元の網目架橋構造を有する有機ゲ ル組成物からなるエアロゲル粒体に、有機材料からなる バインダーと反応固化させたものである。

【0022】また、本発明の請求項2に記載の断熱材 は、分子構造中にウレタン結合を有する有機ゲル組成物 を乾燥して得られるウレタンエアロゲル粒体に、有機ポ リイソシアネートを混合し、反応固化させたことを特徴 としたものであるから、少ないバインダーで優れたエア ロゲルの断熱性能を効果的に発揮させることができる。 10 バインダーである有機ポリイソシアネートは、水分と反

応してウレタン樹脂となってウレタンエアロゲル粒体を 固着させるが、同種材料のこれらは容易に接着が可能で 接着強度も高く、剛性のある断熱材料が生成できる。

【0023】この結果、バインダー量を抑制できるた め、優れたウレタンエアロゲル粒体の断熱特性が支配的 になるのである。また、ウレタンエアロゲル自身も有機 高分子の特徴として架橋網目構造を有するため、剛性が 高く、補強材であるバインダーの大幅低減に寄与してい

【0024】さらには、同種材料のウレタンエアロゲル とウレタン樹脂パインダーからなるため、部材廃棄時の 分別回収は不要であり、ウレタン素材として容易にリサ イクル化が可能である。

【0025】本発明の請求項4に記載する断熱構造体 は、内板と外板間に前記断熱材を配設し、硬質ウレタン フォーム原料で一体発泡してなることを特徴とするもの で、前記断熱材がウレタン素材で形成されており、同種 材料のため、接着強度が高く強度の強い断熱構造体が得 られる。また、得られる断熱材の剛性が高いため、硬質 ウレタンフォームで一体発泡しても発泡圧力でエアロゲ ルがつぶれることもなく、断熱構造体として成型でき る。

【0026】特に、発泡途上でのエアロゲルの崩壊によ る充填性の阻害が原因となる未充填部の発生もなく、断 熱構造体として高断熱性能が発揮できるのである。さら に、断熱構造体が同種材料で構成される結果、部材廃棄 時の分別回収は不要であり、容易にリサイクル化が可能 である。

【0027】本発明の請求項5に記載する断熱構造体 は、分子構造中にウレタン結合を有する有機ゲル組成物 を乾燥して得られるエアロゲル粒体と硬質ウレタンフォ ーム原料を混合した後、内板と外板間に注入充填し、一 体発泡してなる断熱構造体であるため、断熱構造体中に 均一にエアロゲル粒体が分散し、均質な優れた断熱性能 が得られるのである。また、同種のウレタン素材で形成 されるため、部材廃棄時の分別回収は不要であり、容易 にリサイクル化が可能である。加えて、同種材料のた め、接着強度が高く強度の強い断熱構造体が得られるの である.

【発明の実施の形態】本発明の請求項1に記載の断熱材 50 【0028】本発明の請求項6に記載する断熱構造体

は、分子構造中にウレタン結合を有する有機ゲル組成物を乾燥して得られるエアロゲル粒体を不緻布に封入し、 内板と外板間に配設したものであり、耐熱性の高さから、ヒーター部が被断熱貯湯容器の近傍にあるような場合でも、被覆面積の制約はなく、ヒーター部の近傍まで被覆することができる。この結果、電気温水器のような保温貯湯容器に使用した場合、特に、優れた断熱性能を発揮することが可能である。

【0029】本発明の請求項7に記載する断熱構造体は、前記断熱材と釘、配管、配線などの貫通物とからな 10 ることが特徴であり、施工時の設計自由度に優れ、かつ優れた断熱性能が発揮されるものである。これは、エアロゲルは空気の平均自由程以下の微細孔からなり、常圧で優れた断熱性能を発揮するため、エアロゲル内に外部と貫通穴などがあったとしても断熱性能は変化しない。このため、釘、配管、配線などの貫通物の機能を損なうことなく、優れた断熱性能を有するのである。

【0030】以下、実施の形態について、図1から図4を用いて説明する。

(実施の形態1)実施の形態1における断熱材1の一実 20 施例を図1を用いて説明すると、2がウレタンエアロゲルで、ウレタン結合を有するウレタンゲルを超臨界乾燥させて得た粒状エアロゲルである。ウレタンゲルを得る一例としては、水酸基値460mgKOH/gのポリエーテルポリオール100重量部に対して、アミン当量135のポリメリックMDIを115重量部、触媒としてカオーライザーNo.1を2重量部、アセトンを1000重量部混合させ、反応生成物としてウレタンゲルを得ることができる。

【0031】この後、二酸化炭素による超臨界乾燥操作 30 を行い、ナノオーダーを有する超微細多孔質体であるウレタンエアロゲルが得られる。このウレタンエアロゲルは、3次元の網目架橋構造の有機ゲル組成物からなるエアロゲル粒体である。

【0032】3は、バインダーで、アミン当量135のボリメリックMDIを5%と2%の水分をウレタンエアロゲルに均一に混合することによって、ボリメリックMDIと水分が反応硬化した有機材料のウレタン樹脂組成物からなる。反応硬化を促進させるには、5kg/cm2の加圧と100°Cの加温条件で達成することができる。

【0033】このときの断熱材の熱伝導率は、0.00 9w/mKであり、密度は135kg/m3、10%圧 縮強度は、78kPaであった。

【0034】バイダー3は、ウレタンエアロゲル間を接着させるバインダー機能を有しているが、同種のウレタン材料からなっているため、高い接着強度が得られ、剛性の高い断熱材が形成できるのである。

【0035】この結果、バインダー量を抑制できるた。 水を注水し、ヒーター部14の加熱により湯を沸かせてめ、エアロゲルの断熱特性が支配的になるのである。ま 50 貯湯する、外容器11と内容器12間には、ウレタンエ

た、ウレタンエアロゲル自身も有機高分子の特徴として 架橋期目構造を有するため、剛性が高く、補強材である バインダーの大幅低減に寄与している。さらには、同種 材料のウレタンエアロゲルとウレタン樹脂バインダーか らなるため、部材廃棄時の分別回収は不要であり、ウレ タン素材として容易にリサイクル化が可能である。

【0036】(実施の形態2)実施の形態2における一

実施例の断熱構造体4を図2に示す。ウレタンエアロゲルとバインダーから構成されて硬化成形した断熱材1 を、外板5と内板6に形成される空間に配設し、挟持させている。断熱材1は、予め外板5と内板6で形成される空間を有する治具内に充填し、固化させたもので、これを内板6に取付けた後、外板5を形状に沿わせて取り付けることにより、断熱構造体4を得ている。

【0037】断熱材1は、外板5と内板6に形成される空間に沿って隙間なく配設できるため、熱リークもなく優れた断熱性能を断熱構造体4として発揮することができる。特に断熱材1は、ウレタンエアロゲル粒体とバインダーである有機ポリイソシアネートの混合固化によって得られるため、その成形形状は制約なく、厚みの変化や凹凸などが自由に設計できるのである。

【0038】(実施の形態3)実施の形態3における一実施例の断熱構造体7を図3に示す。ウレタンエアロゲルとバインダーから構成されて硬化成形した断熱材1を、内板6の裏面に接着し、外板5で形成される空間に硬質ウレタンフォーム原料を注入し一体発泡を行っている。このため、断熱材1を除く断熱構造体7の内部には硬質ウレタンフォーム8が充填されている。このような複層構造で、断熱材1と硬質ウレタンフォーム8は同種材料で、接着容易で一体発泡による剛性が確保できるため、断熱構造体7の変形はなかった。

【0039】(実施の形態4)実施の形態4における一 実施例の断熱構造体9を図4に示す。ウレタンエアロゲル粒体2と硬質ウレタンフォーム原料を混合し、外板5 と内板6間に注入充填して、断熱構造体9を形成している。混合の重量比率は3:7で、硬質ウレタンフォーム 8中に均一に分散している。

【0040】この結果、曲部等の前記断熱材1を配置できないような個所にもエアロゲル粒体を配置することができ、全体として断熱性能を強化できる。さらには、断熱材1と硬質ウレタンフォーム8は同種材料で、接着容易で層間剥離は起こらず、剛性が確保できるため、断熱構造体7の強度は実用上問題なく、冷凍用断熱壁として使用しても反りなどの変形はなかった。

【0041】(実施の形態5)実施の形態5における一 実施例の断熱構造体10を図5に示す。断熱構造体10 は、外容器11と内容器12と内容器下部13に装着されたヒータ部14から構成されている。内容器12には 水を注水し、ヒーター部14の加熱により湯を沸かせて アロゲル粒体2をパックしたガラス繊維からなる不織布 15を配設している。

【0042】不織布15は、170°Cに達するヒータ 一部に接する内容器下部13まで被覆している。この結 果、フィルム状プラスチックス容器で外被され、溶解の 同題から内容器下部13を被覆できない真空断熱材より も、被覆率25%程が向上し、保温性能が消費電力量換 算で20%改善した。

【0043】(実施の形態6)実施の形態6における一 実施例の断熱構造体15を図6に示す。断熱構造体15 は、断熱構造体4に配管設置用の貫通穴16を加工した ものである。貫通穴16に冷媒配管などの貫通物17を 配設するが、この後工事によっても、断熱構造体15の 断熱性能は変化なく、優れた断熱性能を有することが判 った。比較として、真空断熱材を断熱材1の代わりに配 置し、同様の後工事を行うと断熱性能は1/5に劣化 し、断熱材としての役割発揮ができなかった。

[0044]

【発明の効果】以上述べたところから明らかなように、 橋構造を有する有機ゲル組成物からなるエアロゲル粒体 を有機材料からなるパインダーと反応させると共に、請 求項2に記載の発明は、分子構造中にウレタン結合を有 する有機ゲル組成物を乾燥して得られるウレタンエアロ ゲル粒体に、有機ポリイソシアネートを混合し、反応固 化させたことを特徴とした断熱材であるから、少ないバ インダーで優れたエアロゲルの断熱性能を効果的に発揮 させることができる。

【0045】バインダーである有機ポリイソシアネート は、水分と反応してウレタン樹脂となってウレタンエア 30 ロゲル粒体を固着させるが、同種材料のこれらは容易に 接着が可能で接着強度も高く、剛性のある断熱材料が生 成できる。この結果、バインダー量を抑制できるため、 優れたウレタンエアロゲル粒体の断熱特性が支配的にな るのである。

【0046】また、ウレタンエアロゲル自身も有機高分 子の特徴として架橋網目構造を有するため、開性が高 く、補強材であるバインダーの大幅低減に寄与してい

【0047】さらには、同種材料のウレタンエアロゲル 40 とウレタン樹脂バインダーからなるため、部材廃棄時の 分別回収は不要であり、ウレタン素材として容易にリサ イクル化が可能である。

【0048】請求項4の発明は、内板と外板間に前記断 熱材を配設し、硬質ウレタンフォーム原料で一体発泡し てなる断熱構造体であるから、前記断熱材がウレタン素 材で形成されており、同種材料のため、接着強度が高く 強度の強い断熱構造体が得られる。また、得られる断熱 材の脚性が高いため、硬質ウレタンフォームと一体発泡 しても発泡圧力でエアロゲルがつぶれることもなく、断 50 【図6】本発明の実施形態6における断熱構造体の模式

熱構造体として成型できる。

【0049】特に、発泡途上でのエアロゲルの崩壊によ る充填性の阻害が原因となる未充填部の発生もなく、断 熱構造体として高断熱性能が発揮できるのである。

【0050】さらに、断熱構造体が、同種材料で構成さ れる結果、部材廃棄時の分別回収は不要であり、容易に リサイクル化が可能である。

【0051】請求項5の発明は、分子構造中にウレタン 結合を有する有機ゲル組成物を乾燥して得られるエアロ 10 ゲル粒体と硬質ウレタンフォーム原料を混合した後、内 板と外板間に注入充填し、一体発泡してなる断熱構造体 であるため、断熱構造体中に均一にエアロゲル粒体が分 散し、均質な優れた断熱性能が得られるのである。

【0052】また、同種のウレタン素材で形成されるた め、部材廃棄時の分別回収は不要であり、容易にリサイ クル化が可能である。加えて、同種材料のため、接着強 度が高く強度の強い断熱構造体が得られるのである。

【0053】請求項6の発明は、分子構造中にウレタン 結合を有する有機ゲル組成物を乾燥して得られるエアロ 請求項1に記載の発明は、分子構造中に3次元の網目架 20 ゲル粒体を不識布に封入し、内板と外板間に配設した断 熱構造体であるから、耐熱性の高さから、ヒーター部が 被断熱貯湯容器の近傍にあるような場合でも、被覆面積 の制約はなく、ヒーター部の近傍まで被覆することがで

> 【0054】この結果、耐熱性能の高いウレタンエアロ ゲルの特徴を生かした電気温水器のような保温貯湯容器 に使用した場合、特に、優れた断熱性能を発揮すること が可能である。

【0055】請求項7の発明は、前記断熱材と釘、配 管、配線などの貫通物とからなる断熱構造体であり、施 工時の設計自由度に優れ、かつ優れた断熱性能が発揮さ れるものである。

【0056】これは、エアロゲルは空気の平均自由程以 下の微細孔からなり、常圧で優れた断熱性能を発揮する ため、エアロゲル内に外部と貫通穴などがあったとして も断熱性能は変化しない。

【0057】このため、釘、配管、配線などの貫通物の 機能を損なうことなく、優れた断熱性能を有するのであ る.

【図面の簡単な説明】

- 【図1】本発明の実施形態1における断熱材の模式図
- 【図2】本発明の実施形態2における断熱構造体の模式 図
- 【図3】本発明の実施形態3における断熱構造体の模式 冈
- 【図4】本発明の実施形態4における断熱構造体の模式
- 【145】本発明の実施形態5における断熱構造体の模式 凶

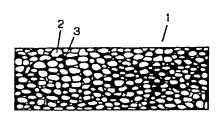
 \square

【符号の説明】

- 1. 断熱材
- 2. ウレタンエアロゲル粒体
- 3. バインダー

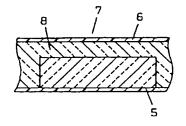
[21]

- ・ ついか で ついり シェアログル 2 ウレタンエアログル 2 かく スプー



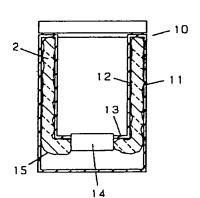
【図3】

7 新熱構造体 8 硬質ウレタンフォーム



【図5】

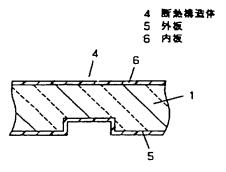
- 10 断熱構造体 15 不兼布



10

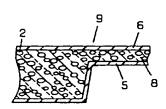
- 4.7.9.10.15.断熱構造体
- 5. 外板
- 6. 内板
- 15. 不織布

【図2】

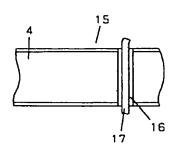


【図4】

9 断熱構造体



【図6】



フロントページの続き

F ターム(参考) 3H036 AA08 AA09 AB18 AB26 AC01 AE13 4F074 AA80 BA34 CA21 CC04Y DA02 DA32 4J034 CE01 DA01 DG00 HA02 HA07 HC12 HC64 HC67 NA03 QB01 QB19 QC01 RA15

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

| ☑ BLACK BORDERS |
|---|
| ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES |
| ☐ FADED TEXT OR DRAWING |
| ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING |
| ☐ SKEWED/SLANTED IMAGES |
| ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS |
| ☐ GRAY SCALE DOCUMENTS |
| ☐ LINES OR MARKS ON ORIGINAL DOCUMENT |
| ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY |
| Потигр. |

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.